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Chemical Analyses for The State of Connecticut Water Resources Commission

Synthetic Organic Materials in Ground Water

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SUMMARY

(1) Chemical analyses were made of ground and surface water samples from Plainville, Connecticut and of industrial process and waste materials from the Marlin-Rockwell Corporation (MRC) plant in that city. The analyses for synthetic detergents, of which alkyl benzene sulfonates (ABS) are the commonest type, were done by the standard methylene blue method. The method does not distinguish between ABS and so-called petroleum sulfonates including ACT0636, a compound used in the machine tool coolant fluid at the MRC plant.

(2) Household well water samples contained no ABS except for a single sample which by analysis showed 0.05 parts per million (ppm).

(3) All samples of MRC process and waste materials were high in "ABS" according to the methylene blue test.

(4) Analyses of constituents of coolant fluid indicated that ACT0636 was the sole material present giving a positive methylene blue test.

(5) Four samples of well water from the MRC plant site gave positive methylene blue tests. Samples from the Plainville Water Company 16-inch well gave no positive tests; one sample of two from the 10-inch well gave a positive test (at the minimum detectable level).

(6) Infrared spectral analysis of a standard ABS sample, of ACT0636, and of material extracted from the MRC 8-inch well indicated .

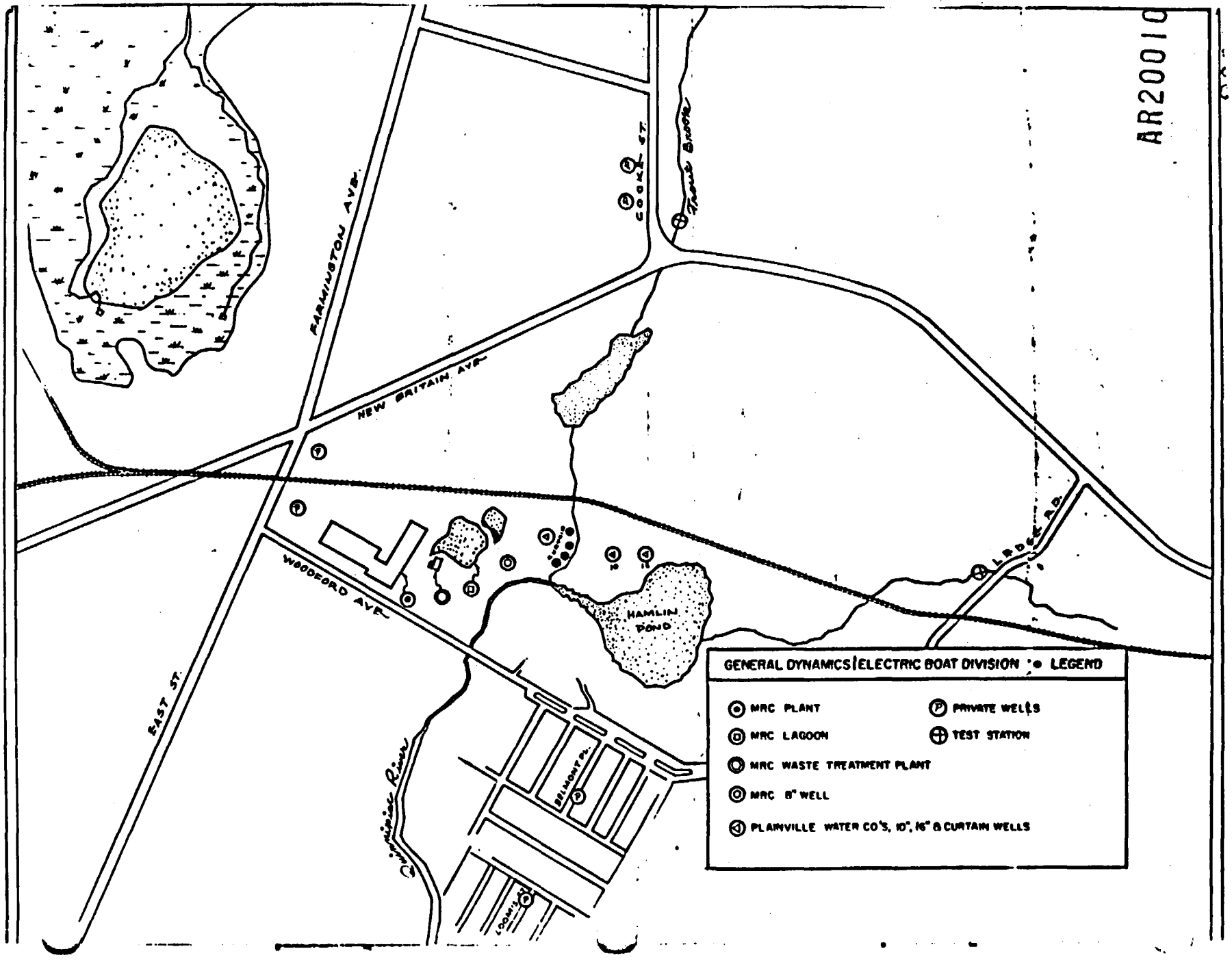
that ABS as such is not present in the well water. The positive methylene blue tests in the well water are due to ACT0636 according to the spectra.

INTRODUCTION

At the request of the State of Connecticut Water Resources Commission, under the contract titled "Investigation and Analyses of Certain Synthetic Chemical Compounds in Ground Water," chemical analyses were conducted on ground water, surface water, and process materials and wastes from the Marlin Rockwell Corporation (MRC) plant in Plainville, Connecticut. This report presents the results of the analyses undertaken.

The purpose of the program was to determine the concentration of alkyl benzene sulfonates (ABS) in surface and ground waters of the area surrounding the plant of the Marlin Rockwell Corporation in order to establish whether reported ground water contamination could be attributed to waste materials of that company or to other sources, such as household septic tanks. According to information supplied by the Water Resources Commision, MRC had discontinued the use of ABS in 1958. Since that time a treatment plant has been put into operation in which combined waste machine coolant fluid, waste cutting oil, and waste water from parts washing machines are treated. Oil is separated from the waste by flotation; the collected oil is burned in the plant boiler. Heavy solids are settled out and used in the plant area for land fill. The waste is then treated by floculation with alum, lime, and bentonite. The sludge formed is separated by flotation and then pumped to a lagoon on the MRC site. The effluent of the treatment plant is discharged to the Quinnipiac River.

A map showing the location wells sampled and other features of the area surrounding the MRC plant is presented as Figure 1. The map is drawn from the United States Geological Survey Topographic Map of the Plainville area, simplified to show only features of interest to this study.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FARMINGTON AVE.
NEW BRITAIN AVE.
WOODFORD AVE.
EAST ST.
COOKE ST.
Trout Brook
HAMLIN POND
LORD RD.
Quinnipiac River
BELMONT PL.
GENERAL DYNAMICS/ELECTRIC BOAT DIVISION • LEGEND
MRC PLANT
MRC LAGOON
MRC WASTE TREATMENT PLANT
MRC 8" WELL
PLAINVILLE WATER CO'S, 10", 16" & CURTAIN WELLS
PRIVATE WELLS
TEST STATION

METHODS AND MATERIALS

Colorimetric Method

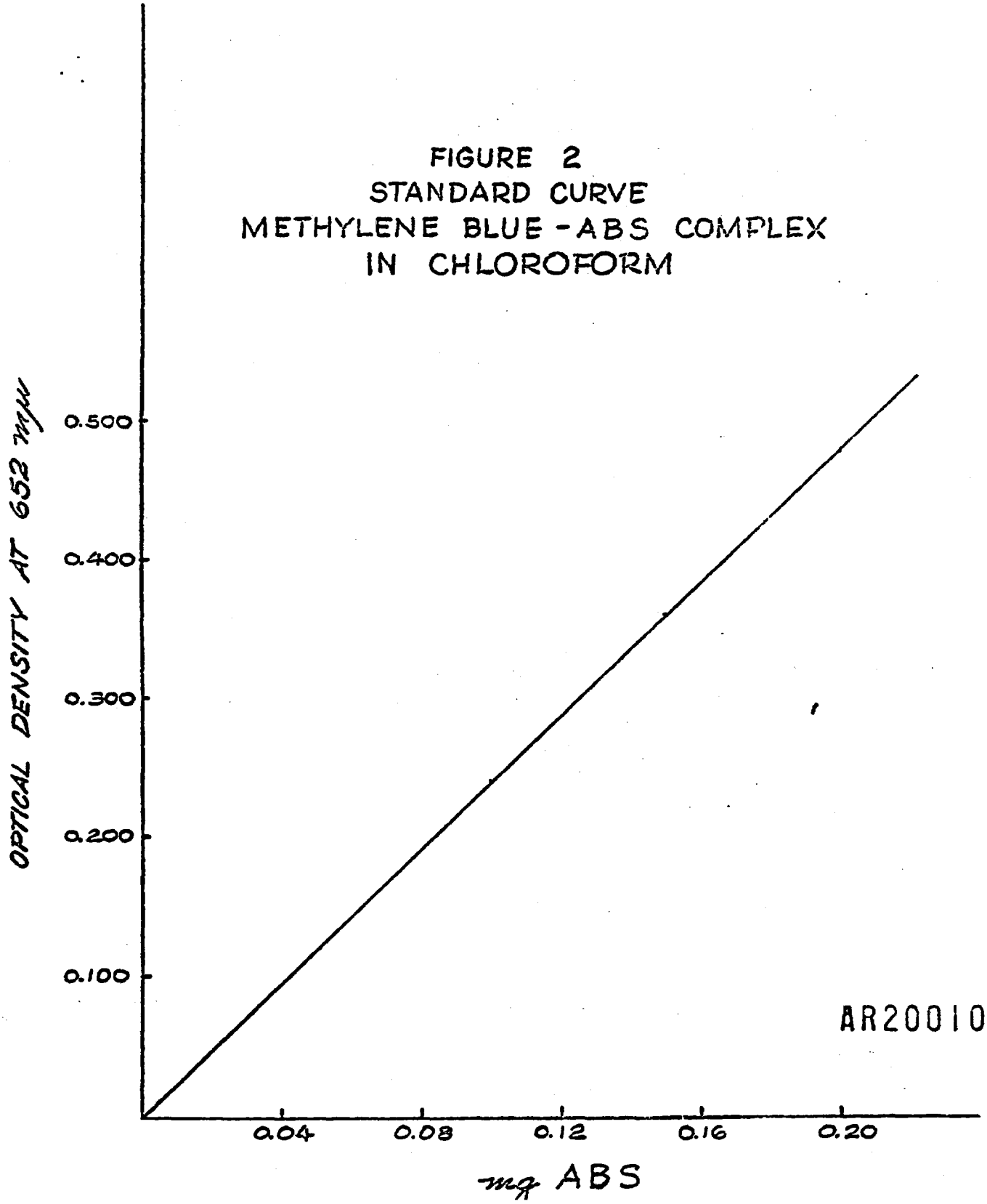
The standard methylene blue method for the determination of surface active agents was used for the quantitative analysis of ABS. The method of analysis is based on the principle that methylene blue forms a chloroform-soluble salt with anionic surfactants, which include not only ABS but also alkyl sulfates such as petroleum sulfonates. Extraction of the salt was accomplished by using a separatory funnel. The intensity of the blue color of the salt was measured in a spectrophotometer at 652 millimicra. The color was proportional to the amount of ABS present in standard samples. (See page 246, Standard Methods for the Examination of Water and Waste Water, 1960.)

Standard ABS was received from the Association of American Soap and Glycerine Producers. It was from Lot #3, June 1961, and contained 54.8% ABS; with the remainder being Na_2SO_4. In order to prepare a standard solution of "100% activity" at the level of 1 gm/liter, 1.8248 gms were dissolved in water and diluted to one liter. A standard curve was made in the range of 0.05mg to 0.2mg (see Figure 2) using measured aliquots of a 1:100 dilution of the stock solution. Standard samples at one or more levels were run with each set of analyses.

Preliminary Analyses

Two samples of well water which were suspected to be contaminated with surfactant were obtained from the Groton, Conn. area. To check the reliability and sensitivity of the methylene blue method, preliminary analyses were conducted on these samples. ABS in one of the samples

FIGURE 2
STANDARD CURVE
METHYLENE BLUE - ABS COMPLEX
IN CHLOROFORM



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was determined to be 0.16 mg/liter, and in the other, 0.44 mg/liter. In order to check for the presence of interfering materials in the ground water, 8ml of standard solution containing 0.08mg ABS were added to a 100-ml sample of well water containing 0.016mg ABS by analysis. The combined sample was found to contain 0.097mg; in other words, the effect was simply additive, within the limits of sensitivity for the method.

Preliminary Samples from Plainville

On October 27, 1961, three samples were collected by Dr. R. J. Benoit of Electric Boat Division:

1) MRC coolant fluid on-stream (milky white, petroleum smell)
2) MRC 8-inch well (cloudy)
3) MRC waste water (very cloudy, petroleum smell)

After the correct dilution ranges were found, analyses for ABS were performed and the results shown in Table I were obtained.

In order to check coolant and waste water for interfering substances, 10ml of standard solution containing 0.100mg ABS were added to 5ml of diluted coolant containing 0.046mg ABS by analysis; 5ml of standard solution containing 0.050mg ABS were added to 10ml diluted waste water containing 0.048mg ABS by analysis. In both instances, the effect was simply additive.

TABLE I

ABS CONTENT OF PRELIMINARY SAMPLES FROM THE PLAINVILLE AREA

Sample	Aliquot (ml)	ABS in Aliquot (mg)	ABS in Sample (mg/l)
MRC 8-inch Well	25	0.050	2.00
	50	0.104	2.08
MRC Coolant Fluid (Diluted 1:100)	10	0.090	900
	20	0.187	935
MRC Waste Water (Diluted 1:10)	10	0.048	48.0
	30	0.124	41.3

Further Tests with Coolant Fluid

A series of analyses were made to determine the substance responsible for ABS activity of coolant fluid. According to information from MRC, coolant stock mix is composed of:

19.4% ACTO 636 (An Esso Corporation octadecyl sulfonates product)
0.6% Napthenic Acid
80.0% Coray 40

The coolant fluid contains one part of the above mixture to forty parts of water.

Samples of materials contained in coolant were received from MRC.

1) Esso Napthenic Acids (dark brown liquid)
2) Esso Coray 40 (clear, yellow liquid)
3) Esso ACTO 636 (dark brown, sticky, clear paste)

For the qualitative determination of ABS activity, one drop of each material was added to a small amount of acetone and then diluted with water to 50 ml. Methylene blue was added and 50-ml samples were extracted with chloroform in the usual manner. Napthenic acid and Coray 40 gave a negative test; ACTO 636 gave a positive test.

Quantitative Test for ABS Activity of ACTO 636

Twenty milligrams of ACTO 636 were weighed out and dissolved in a small amount of acetone. The solution was then transferred to a 100-ml volumetric flask, which was filled to volume with water. One milliliter of this solution, containing 0.2 mg of ACTO 636, gave an optical density of 0.185 units, or 0.084 mg active substance; consequently, ACTO 636 gives 42% ABS activity on a weight basis.

An artificial sample of coolant fluid was prepared according to the recipe given above.

The calculated ABS activity of artificial coolant is 2,100 mg/l, but the on-stream coolant sample from MRC had only about 900 mg/l by analysis. Determination of total solids of both coolant samples was accomplished by drying 3 ml of each in aluminum dishes at 95°C. The on-stream sample gave 18.4 mg/3 ml, and the artificial coolant gave 36.0 mg/3 ml, indicating that the on-stream coolant sample was only one-half strength relative to the recipe; or in other words, the activity of ABS was the same in the on-stream sample and the artificial sample on a solids content basis.

In summary, ACTO 636 accounts quantitatively for the ABS activity of coolant fluid.

ABS Content of Definitive Samples

Two sets of definitive samples were collected and analyzed. The first set was delivered to the Electric Boat Research Annex by Mr. Snow of the Water Resources Commission on November 14, 1961. Appropriate dilution ranges and/or aliquot sizes were established. Analyses were run on November 15, 1961. Results for the first set are given in Table II. The second set of definitive samples was received on November 28, 1961. Results are given in Table III.

The results from Tables II and III have been regrouped by type of sample in Tables IV, V, and VI.

Table IV gives the results of analyses of all well-water samples. Ten samples had no measurable ABS content and one sample from a well at 72 Loomis St. contained 0.05 mg/l. One of four samples from the Plainville Water Company contained 0.05 mg/l. The MRC 8-inch Well contained from 1.1 to 2.0 mg/l.

Table V shows the ABS levels of surface waters; Trout Brook and the Quinnipiac River, on two different dates.

Table VI shows the analyses of MRC process materials and wastes. They are all positive for ABS.

TABLE II

SAMPLES COLLECTED NOVEMBER 14, 1961

Source	Description	Aliquot (ml)	ABS in Aliquot (mg)
Well, 89 Cooke St.	Clear	400	nd*
Well, General Electric Co. Woodford Plant	"	"	"
Well, 68 Belmont St.	"	"	"
Well, Liberty Mobile Homes	"	"	"
Well, 79 Loomis St.	"	"	"
16-inch Well, Plainville Water Co.	"	"	"
10-inch Well, Plainville Water Co.	"	"	"
Trout Brook at New Britain Ave.	Cloudy	"	0.028
Quinnipiac River at Ledge Road	"	100	0.094
MRC 8-inch Well	"	50	0.058
MRC Lagoon	"	10	0.090
MRC Waste Oil (Diluted 1:25)	White Opaque	1	0.112

*nd: Analyzed for but not detected; such samples contain less than 0.01 mg.

TABLE III

SAMPLES COLLECTED NOVEMBER 28, 1961

Source	Description	Aliquot (ml)	ABS in Aliquot (mg)
16-inch Well, Plainville Water Co.	Clear	400	nd
10-inch Well, Plainville Water Co.	"	"	0.02
2-inch Curtain Well, Plainville Water Co.	"	"	nd
Well, Liberty Mobile Homes	"	"	"
Well, G.E. Woodford Ave. Plant	"	"	"
Well, G.E. North Plant	"	"	"
Well, 89 Cooke St.	"	"	"
Well, 79 Loomis St.	Yellowish	"	0.020
Trout Brook at New Britain Ave.	Cloudy	"	0.020
Quinnipiac River at Ledge Road	Kerosene Smell	200	0.034
MRC Waste Water (Diluted 1:25)	Chalky; Oily	3	0.051
MRC Sludge (Diluted 1:20)	Thick Grey	1	0.088
" 1:100)		5	0.071, 0.082
MRC Waste Treatment Plant Effluent	Yellow, Clear	3	0.044
		10	0.135
MRC Lagoon	Cloudy	10	0.186
MRC 8-inch Well	Yellowish	50	0.096
		100	0.186

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TABLE IV

ABS CONTENT OF WELL WATER SAMPLES

Source	Date Collected	ABS(mg/l)
Cooke St.	11-14-61	nd
Cooke St.	11-28-61	"
68 Belmont St.	11-14-61	"
Liberty Mobile Homes	11-14-61	"
Liberty Mobile Homes	11-28-61	"
G.E. Woodford Plant	11-14-61	"
G.E. Woodford	11-28-61	"
G.E. North Plant	11-28-61	"
79 Loomis St.	11-14-61	"
79 Loomis St.	11-28-61	0.05
10-inch Well, Plainville Water Co.	11-14-61	nd
10-inch Well, Plainville Water Co.	11-28-61	0.05
16-inch Well, Plainville Water Co.	11-14-61	nd
16-inch Well, Plainville Water Co.	11-28-61	"
2-inch Curtain Well, Plainville Water Co.	11-28-61	"
MRC 8-inch Well	10-27-61	2.04
MRC 8-inch Well	11-14-61	1.16
MRC 8-inch Well	11-28-61	1.86
MRC 8-inch Well	11-28-61	1.92

TABLE V

ABS CONTENT OF SURFACE WATER SAMPLES

Source	Date Collected	ABS (mg/l)
Trout Brook at New Britain Ave.	11-14-61	0.07
Trout Brook at New Britain Ave.	11-28-61	0.05
Quinnipiac River at Ledge Road	11-14-61	0.94
Quinnipiac River at Ledge Road	11-28-61	0.17

TABLE VI

ABS CONTENT OF MRC PROCESS MATERIALS AND WASTES

Source	Date Collected	ABS (mg/l)
Coolant	10-27-61	900, 935
Lagoon	11-14-61	9.0
Lagoon	11-28-61	18.6
Waste Oil	11-14-61	2810
Waste Water	10-27-61	48.5, 41.3
Waste Water	11-28-61	425.0
Sludge Sample	11-28-61	1760, 1420, 1640
MRC Waste Treatment Plant Effluent	11-28-61	14.6, 13.5

ABS and Solids Content of MRC Waste Water

The wide difference between the two samples of waste water in Table VI was noted. Repeat analyses confirmed the original results. In order to determine the extent of the day-to-day variation, a third set of sample was collected at the MRC waste treatment plant on January 4, 1962. The set included two samples of waste water, one collected from the waste tank a few minutes after the other, and a sample of waste, mostly oil, from the surface of the settling tank. The oil sample was found to contain 2200 mg/l ABS. The first waste water sample collected was visibly more dilute than the second.

The total solids content of the two waste water samples and of the original two waste water samples was determined by evaporating 3-ml aliquots at 95°C and weighing the residues. The weights of the residues and the corresponding ABS contents were as follows:

Sample Collected	Weight of Residue (mg)	ABS Content (mg/l)
10/27/61	4.5	48.0, 41.3
11/28/61	9.4	425
1/4/62 (#1)	1.4	36
1/4/62 (#2)	5.0	70

It is clear that the ABS content is not simply proportional to the solids content in waste water. It is equally clear that samples high in total solids are high in ABS.

The results in Tables II and III show that some ABS-active material is present in ground and surface waters of the Plainville area. Furthermore, the MRC process materials and waste have been shown

to be very high in ABS activity. These analyses indicate that ACTO 636 accounts qualitatively for the ABS activity of coolant fluid. It is reasonable to conclude that the same substance likewise accounts for the ABS activity of MRC waste materials.

The methylene blue method is not specific for ABS; in order to distinguish between ABS and other materials (like ACTO 636) which give a positive methylene blue color, infrared absorption spectra were made.

Infrared Analysis of ABS, ACTO 636 and Well Water

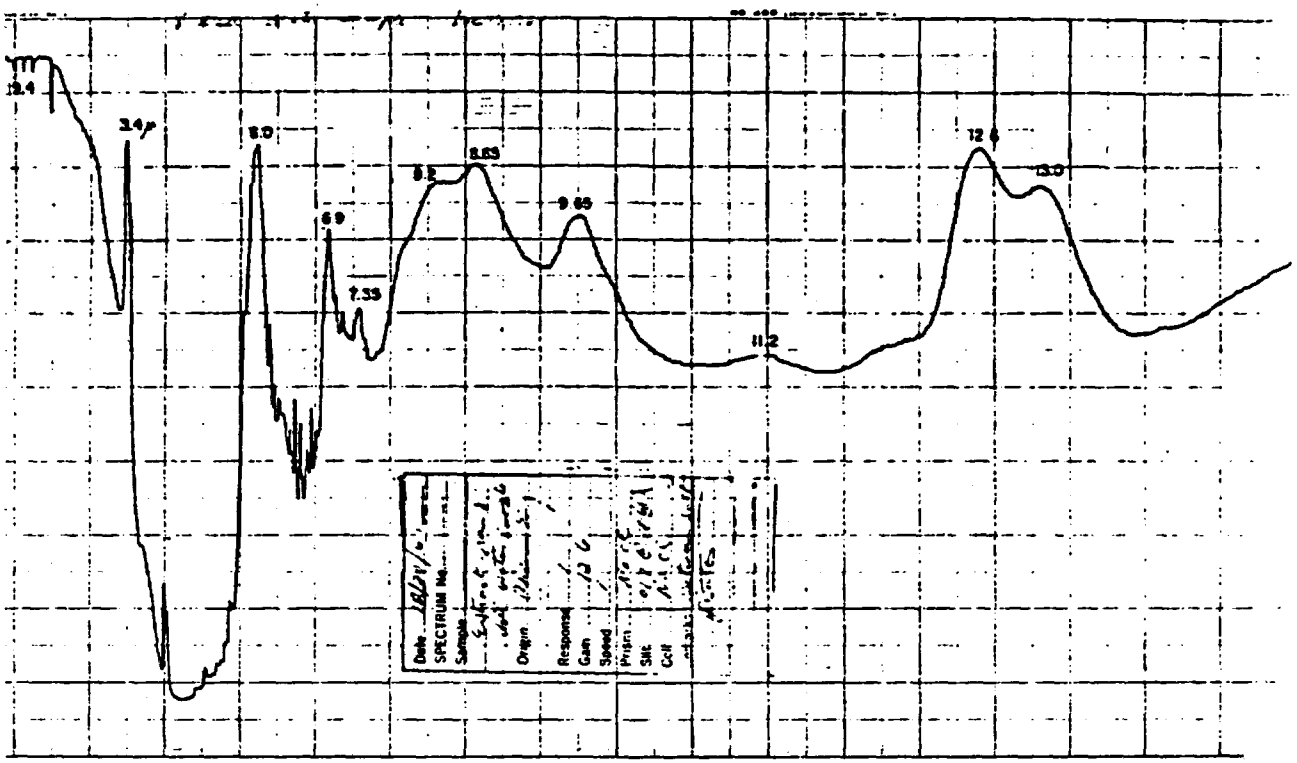
The infrared absorption method of Sallee* is accepted as a tentative standard. This method allows the distinguishing between ABS and other substances giving a positive methylene blue test.

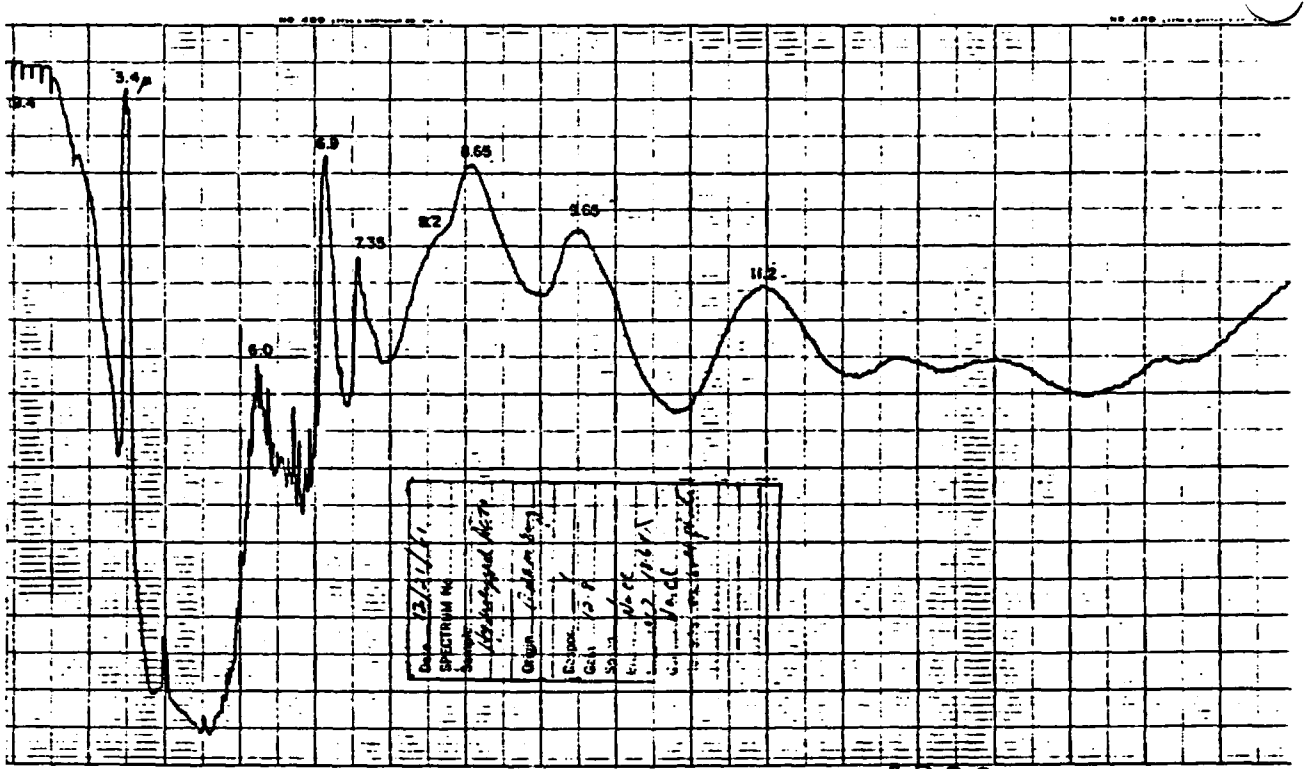
Method of Extraction of Ground Water

Sallee's method can be described briefly as follows:

> Twenty liters of ground water are passed through a column of charcoal. The adsorbed material is eluted with a solvent and concentrated by evaporation. It is then hydrolyzed with hydrochloric acid, extracted with petroleum ether, and complexed with 1-methylheptylamine. The absorption spectrum of the amine complex can be taken as the complex can be hydrolyzed with dilute alkali and the spectrum of the free ABS taken.

*See "Determination of Trace Amounts of Alkyl Benzene-sulfonates in Water," E.M. Sallee. Analytical Chemistry. Vol 28 p. 1822 1956.





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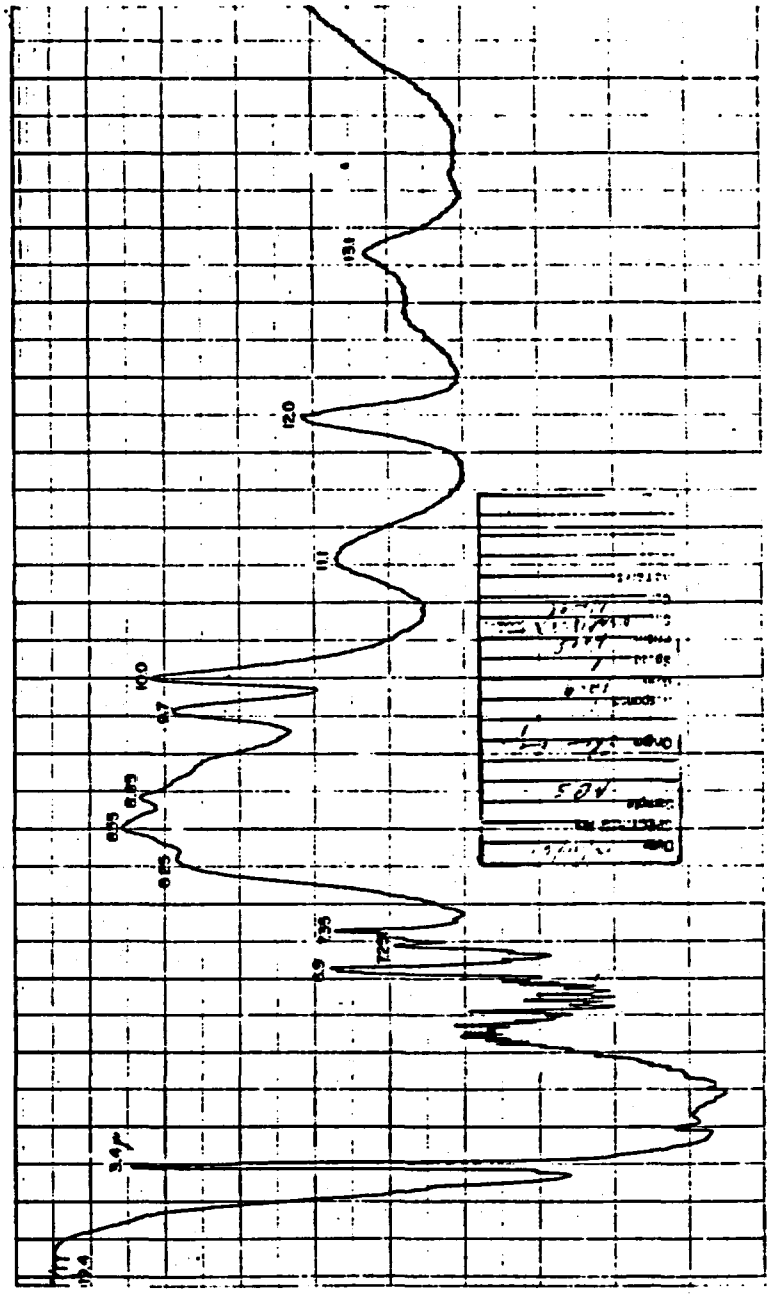

In our work, Sallee's method was modified in the following manner:

> The original method requires that each of four sections of charcoal from the column be extracted twice with methanol-benzene and the extracts combined. We extracted each section once, with methanol-toluene, and then extracted all sections combined with the same solvent mixture.

Spectra were made on standard ABS hydrolyzed with acid, ACTO 636 hydrolyzed with acid, and the extract of well water prepared as described above. All the hydrolyzed residues had the same pleasant odor.

The spectrum of standard ABS (see following page, upper spectrum) compares favorably with the published spectra for ABS reference standard and extract of Ohio River water (Sallee, 1956). In all three spectra, similar peaks occur at 3.4, 8.55, 8.85, 9.7, 9.9 12.0, and 13.2μ. The spectra are only superficially similar to the spectrum of extract of MRC well water (middle spectrum).

The spectrum of the extract MRC well water has sharp peaks at 3.4, 6.0, 6.9 and 7.35, a broad peak at 8.2-8.65, and a characteristic peak at 9.65μ.

The spectrum of hydrolyzed ACTO 636 (lower spectrum) has a broad peak extending from 8.2-8.65; it also has the characteristic peak at 9.65μ. The similarity of spectra of MRC well water extract and hydrolyzed ACTO is obvious.

Evidence from the spectrographic measurements suggests that ABS, as such, does not exist in the MRC well water, but rather that the ABS activity of the well water, as determined by the methylene blue method, is derived from ACTO 636.